

**THE INVESTIGATION OF ACTIVATED CARBON PREPARED FROM
PALM SEEDS POWDER (*Bactris gasipaes*) FOR REMOVAL OF
METHYLENE BLUE FROM WASTEWATER**



M.Sc. Thesis

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June 2017

Adama, Ethiopia

**THE INVESTIGATION OF ACTIVATED CARBON PREPARED FROM
PALM SEEDS POWDER (*Bactris gasipaes*) IN THE REMOVAL OF
METHYLENE BLUE FROM WASTEWATER**

**In Partial Fulfillment of the Requirements for the Degree of
Master of Science in Applied Chemistry (Analytical Chemistry)**

**A Thesis Submitted to Program of Applied Chemistry, the School of Applied
Natural Science, Adama Science and Technology University**

By

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June, 2017

ASTU, Adama, Ethiopia

Adama Science and Technology University
SCHOOL OF APPLIED NATURAL SCIENCE

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DEDICATION

I dedicated this project manuscript to my mother, Jemila Tufa for nursing me with affection, love and for her dedicated partnership in success of my life.

STATEMENT OF THE AUTHOR

By my signature below, I declare and affirm that this thesis is my own work. I have followed all ethical and technical principles of scholarship in the preparation, data collection, data analysis and completion of this graduate project. Any scholarly matter that is included in the thesis has been given recognition through citation.

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LIST OF SYMBOLS ABBREVIATIONS

MB	Methylene Blue
PSP	Palm Seeds Powder
Ppm	Part per million
ppb	Part per billion
FT-IR	Fourier transforms infrared
UV/VIS	Ultraviolet visible
q	The Amount of Adsorbate per gram of adsorbent (mg.g-1)
q_e	The Amount of Adsorbate per gram adsorbent at equilibrium (mg.g-1)
q_t	The Amount of Adsorbate per gram of adsorbent at any time
q_m	Equilibrium adsorption capacity using model
q_{max}	Maximum adsorption capacity (mg/g)
t	Time (min)
T	Temperature (K)
COD	Chemical oxygen Demands
C_e	Amount of MB in solution, ppm (mg/L)
C_{ads}	Amount of MB adsorbed ppm (mg/L)
C_0	Initial concentration of MB, ppm (mg/L)
AC	Activated carbon
L	Litre
M	Molar

BIOGRAPHICAL SKETCH

The author was born in October 16, 1980 G.C, in East Arsi Zone, Munesa Woreda, Kote Kebele, and Oromia Region. He attended his elementary and secondary school education at Gujicha elementary school and Kersa secondary school respectively. Then, in 2003 he joined Adama Teachers College and received his diploma in Chemistry in July 2003. After his graduation, he was employed by the Oromia Regional State Education Bureau as junior school Chemistry teacher in Kersa secondary school and after serving for 10 years, in 2006 he joined Addis Ababa University through summer program and received his Bachelor of Education Degree (BED) in Chemistry in September 10. In 2014, he joined the post graduate program at Adama Science and Technology University to pursue his M.Sc. Study in Analytical Chemistry.

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ABSTRACT

This thesis aimed to investigate the potential of activated carbon (AC) prepared from palm seeds powder (PSP) as an alternative and environmental friendly adsorbent for the treatment of dye containing wastewater. The results indicate that AC prepared from PSP could be employed as low cost alternatives to commercial activated carbon in waste water treatment for the removal of basic dyes. This low cost and effective removal method may provide a promising solution for the removal of methylene blue dye from wastewater. Kinetic and thermodynamic studies were investigated, pseudo second order was observed to be the most suitable to describe the adsorption process. Values obtained from thermodynamic analysis show that the adsorption process is endothermic, spontaneous and chemisorptions in nature.

Keywords:, Wastewater, Methylene Blue, activated carbon, Palm seed, Dye removal, Dye adsorption

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1.INTRODUCTION

Water is essential for the survival of all living organisms. Today contamination of freshwater systems with a wide variety of pollutants is a subject of great concern. Out of all the contaminants present in industrial effluents, dyes are an important class of pollutants and can be identified by even human eye. Dyes are used as coloring agents in a variety of industries such as textiles, food, paper, rubber, plastics, cosmetics, leather; *etc.* The discharge of wastewater from these industries to water resources causes unavoidable problems due to the toxic and unpleasant nature of dyes. The presence of dyes in water in trace amount is undesirable because most of them are toxic, mutagenic and carcinogenic (Soni, *et al.*, 2012). Dyes also prevent light penetration and thereby reduce photosynthetic activities of water streams and disturb the aquatic equilibrium. Thus, removal of dyes from wastewater before discharge is a challenging task.

MB, a cationic dye, is most commonly used as the coloring agent for cotton, wool and silk. It is also used as a staining agent to make certain body fluids and tissues easier to view during surgery and diagnostic examinations. The medical applications of MB, also include the treatment of methaemoglobinemia and cyanide poisoning. In spite of several applications, this dye has a number of negative impacts on human beings and animals; such as irritation of mouth, throat, esophagus and stomach with symptoms of nausea, abdominal discomfort, vomiting and diarrhea. Skin contact may cause mechanical irritation resulting in redness and itching. Thus, removal of MB dye from wastewater is of great concern from human and environmental point of view as well (Sarici-Ozdemir 2014).

Several techniques like flocculation, adsorption, oxidation, electrolysis, biodegradation, ion-exchange, photo catalysis have been employed for the removal of dyes from wastewater (Bhatnagar and Sillanpa, 2010). Amongst the various techniques, adsorption has received considerable attention due to its several advantages in terms of cost, ease of operation, flexibility and simplicity of design and insensitivity to toxic pollutants (Crini, 2005; Rafatullah 2010). Among the variety of adsorbents, activated carbon may be logically the most preferred adsorbent for the removal of dyes because of its excellent adsorption ability (Robinson *et al.*, 2010). However, widespread use of activated carbon is restricted because of its high cost (Al-Degs *et*

al.,2009). Thus, attention has shifted to find efficiency and cheaper alternatives of activated carbon. Natural materials, agricultural and industrial wastes and biosorbents represent potential alternatives. A number of non-conventional and low cost adsorbents have been proposed by many workers for the removal of dyes (Crini, 2006; Robinson, 2001, Gupta and Suhas, 2009 and Bhatnagar and Sillanpa 2010). These include agricultural waste products saw dust (Agarwal ,2010), bark (Morais *et al.* ,1999), industrial waste products metal hydroxide sludge (Netpradit 2003), red mud (Wang,2005), fly ash (Mohan *et al.*,2002), clay materials bentonite (Espantaleon *et al.*,2007), di- atomite (Al-Ghouti *et al.* ,2003) , zeolites (Ozdemir *et al.*, 2004, Armagan *et al.*,2004) ,*etc.*

Many low cost adsorbents have been reported in literature for the adsorption of MB. However, literature survey reveals that so far no considerable effort has been made to study the treatment of MB, dye by activated carbon prepared from PSP. Therefore in this research project the efficiency of AC prepared from PSP as an adsorbent will be investigated for removing MB, dye from wastewater due to its low cost, easily available etc.

1.1 Statement of problem

Wastewater containing dyes is undesirable since tiny amount of dye material destroy the aesthetic values of water. It is necessary to effectively treat effluent containing dyes due to the environmental and toxicology threats posed to human and aquatics.

Many techniques such as adsorption, ion exchange, coagulation flocculation, precipitation and chemical oxidation have been used for removing dyes from wastewater. However, some of these techniques are inefficient or expensive to treat both diluted and concentrated pollutants (Vadivelan *et al.*, 2005). Adsorption technique has been found to be a superior separation and purification method to other methods due to its easy nature, low cost, high selectivity, and high efficiency (Ozde *et al.* s,2014).

Numerous low cost adsorbents such as bentonite, fruit peel, papaya seeds, orange peels, saw dust, walnut shells, zeolites synthesized from fly ash, swelling clay, and cedar saw dust and crushed bricks have been used for removal of MB, from wastewater. Some of the adsorbent

reported have been remarkable to treat contaminated wastewater due to their high cost, inefficient, large surface areas and porosity to remove acidic and basic dyes from wastewater. AC prepared from palm seeds powders has been found to be a versatile adsorbent, which can remove diverse type of pollutants such as metal ions, dyes, phenol and a number of other organic and inorganic compounds and bio-organisms. However, its use is sometimes restricted to higher cost. Due to higher cost of AC, attempts are being made to regenerate the spent activated carbon. Chemicals as well as thermal regeneration methods are used for this purpose. However, these procedures are not very cheap and also produce additional effluents and result in considerable loss of adsorbents. Therefore, in situation where cost factors play a major role, scientists are looking for low cost adsorbent for control of water pollution. As such for quite some, efforts have been directed towards developing low cost adsorbents. Wide variety of materials has been investigated for this purpose and they can be classified into three categories. i. natural materials ii. Agricultural waste iii. Industrial wastes. These materials are generally available free of cost or cost little as compare to others activated carbons. However their regeneration and desorption kinetics is questionable (Ahmad *et al.*, 2012). Therefore, in this research seed of palm powder will preferred due to its low cost, easily available and efficient adsorbent that can effectively remove acidic and basic dyes from wastewater (Ashiq *et al.*, 2012). To the best of our knowledge there is no any research has been done on the seed of palm powder for removal of MB dye from wastewater in Ethiopia. In Ethiopia there is a lot of textile, leather industries. So it is very important to treat the dyes from the wastewater that reused from the factories.

1.2 Objectives of the Research

1.2.1 General objective

The main objective of this research project is to use the activated carbon (AC) prepared from seeds of palm powder (PSP) as an adsorbent for removing MB, dye from wastewater using the adsorption process.

1.2.2 Specific objective

The specific objectives of this research project are

- To investigate the adsorptive capacity of the adsorbent,

- To examine the influence of different parameters such as pH, adsorbent dosage concentration, contact time, temperature through adsorption process,
- To study the kinetics and thermodynamics properties for the adsorption process, and
- To examine the removal of MB, dye from wastewater by using activated carbon prepared from palm seeds powder (PSP) as adsorbent.

1.3 Scope of Study

The scope of this study is to test waste water for the removal of methyl blue using palm seeds powder as adsorbent. Applications of AC are enormous. It's important use is for gasoline vapor emission control canisters in automobile. AC can act as a filter material in air cleaning filters for removal of gases and vapors in the industrial environment. Especially impregnated grades are used in cigarette filters to absorb some of the harmful components of tobacco, and as the catalyst or carrier of catalytically active substances. Heavy metal ions such as mercury, lead and cadmium in drinking waters are very dangerous even in trace amount, and adsorption method for removing these ions can be essential for water and waste water contaminated by heavy poisonous metal ions. For example lead, cadmium, mercuric ions all are very toxic and carcinogenic. Lead is also a cumulative metabolic poison, acting as a mutagen when adsorbed in excessive amounts. These ions cannot be removed from water with classic physical or chemical treatments completely. Activated carbon can be used for removal of poisonous heavy metal ions from aqueous solutions. Adsorption in this case is due to the surface complex formation between the metal ions and the acidic surface function group of AC. Adsorption is due to the surface complex formation between the metal ions and the acidic surface function group of AC. The removal efficiency is influenced by various factors, such as solution concentration, solution pH, ionic strength, nature of adsorbate, adsorbent modification procedure, Physical properties (surface area, porosity), and the chemical nature of AC. Batch studies were conducted using MB.

2. LITERATURE REVIEW

2.1 Palm Seeds

Palm tree are regarded as international socio-economic plants. The palms belong to the Arecaceae sub-group, which are a botanical family of perennial shrubs, and trees commonly known as palm trees. They are flowering plants, the only family in the monocot order Arecaceae and mostly restricted to tropical and warm temperate climates. Most palms are distinguished by their large, compound, evergreen leaves arranged at the top of an unbranched stem. However, many palms are exceptions, and in fact exhibit an enormous diversity in physical and morphological characteristics. Numerous common products and foods are derived from palms, and palms are also widely used in landscaping for their exotic appearance, making them one of the most economically important plants. However, little information has been documented on the utilization of the palm seeds for water treatment. This prompted us to evaluate the potential of palm seeds as alternative adsorbent (Dewier *et al.*,2011).



Figure 2. 1 Palm tree plant

2.2 Uses of Palm Tree

There are so many more palm tree uses than just providing shade for you on a hot Caribbean beach. It is one of the most widely used trees on the planet. There are lots of different kinds used in commercial growing operations. Everything on the tree even some roots is reused in some way, shape or form. But the other uses for various types of palm tree fruit are for oil, biodiesel, wax, jelly, wine and palm heart for salads. Now there's what is called vegetable ivory being made from the seed of a palm in South America. Even natural health supplements like Saw Palmetto and the Acai berry come from palm trees (Ahmad *et al.* , 2012).

2.3 Dye Contaminated Wastewater

Wastewater containing dyes can be described to possess low chemical oxygen demand (COD) and high alkalinity. The treatment of this effluent may be difficult due to the complex aromatic structures of dyes.

Dyes can be categorized as:

- Anionic (direct, acid and reactive dyes)
- Cationic (basic dyes)
- Nonionic (disperse dyes) (Namasivayam ,2001).

2.4 Dye Treatment Process

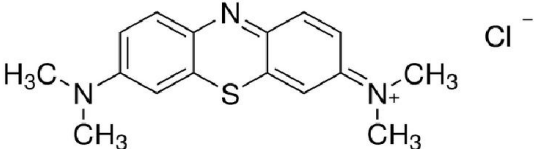
Several treatment techniques have been utilized for removal of dyes from aqueous solution such as: photocatalytic degradation, sonochemical degradation, electrochemical degradation, ultra filtration, adsorption/precipitation processes, integrated chemical biological degradation etc. As the artificial dyes in aqueous solution cannot be decolorized by conventional methods effectively, the adsorption of artificial dyes on cheap and effective solid supports has been reported to be suitable and promising (Rafatullah *et al.* ,2013).

2.5 Methylene blue in the Environment

MB, is a cationic dye and regarded as significant threat to human and biota due to its carcinogenic and mutagenic properties. It has been widely used in coloring paper, wools, as biological stains and dyeing cottons (Sarici-Ozdemir, 2014). Therefore, it is one of environmental concern to treat MB, containing effluent before being discharged into fresh streams.

2.5.1 Properties of Methylene Blue

Table 2. 1 phsical properties of Methylene blue

Molecular weight (M.W)	319.85222 g/mol
Molecular formula	C ₁₆ H ₁₈ N ₃ SCl
Solubility	Slightly soluble
Melting point	100-110 °C (with decomposition)
Appearance	Dark green
Structure of MB	3, 7-Bis (dimethylamino) phenothiazin-5-ium 

2.5.2 Uses of Methylene Blue

Methylene Blue (MB) has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, *etc.* MB, is also used in microbiology, surgery, diagnostics, trace analysis of anionic surfactants present in aqueous streams and as a sensitizer in oxidation of organic pollutants (Bielska, and Szymanowski *et al.*, 2006). Though MB dye is strongly hazardous, it can cause some harmful effects. Acute exposure to MB dye will found cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in human (Kumar *et al.* , 2005). Due to low biodegradability of dyes a conventional biological treatment process is not very effective in treating a dye wastewater

2.6. Kinetics of the Adsorption Isotherms

2.6.1 Adsorption process of dyes

Adsorption is the transferring of adsorbate (dyes) from the liquid phase onto the surface of a solid (adsorbent). The term adsorption is often confused with absorption. Absorption refers to a phenomenon where something is taken up through the bulk, such as a sponge absorbs water where as adsorption refers to a phenomenon where something is taken up only at the surface, such as carbon powder adsorbs a dye. The general term for absorption and adsorption is sorption. A substance that under goes adsorption is referred to as the adsorbate, and the solid that adsorbs a liquid is adsorbent (Itodo and Itodo, 2010). In adsorption process of dye on the solid surface, the dye species migrate to words the surface of the adsorbent. This type of migration proceeds till the existence of concentration gradient of the adsorbate species in the bulk of the solution. Once equilibrium is attained, the migration of the solute species from the solution stops. At this situation, it is possible to measure the magnitudes of distribution of the solute species between the liquid and solid phases.

2.6.2 Types of adsorption

Basically, there are two types of adsorption. These are (1) Physical adsorption (Physisorption) and (2) Chemical adsorption (Chemisorptions). Physical adsorption occurs when weak interparticle bonds exist between the adsorbate and adsorbent. Examples of such bonds are Vanderwaals forces. Whereas Chemical adsorption occurs when strong interparticle bonds are present between the adsorbate and adsorbent due to exchange or sharing of electrons. Examples of such bonds are covalent bonds (Allen and Koumanova 2005).

2.6.3 Pseudo first order equation

The adsorption kinetic described by the Lagergren pseudo first order equation describing the adsorption rate based on the adsorption capacity. The differential pseudo first order equation generally expressed as follows (Baek *et al.* ,2010).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots \dots \dots (1)$$

Where k_1 is the rate constant of the pseudo first order adsorption (min^{-1}), q_t - the amount of MB, adsorbed onto PSP at different times (mg/g), and q_e is the amount of methylene blue adsorbed onto palm seeds powder at the equilibrium (mg/g) then after taking integral for above equation it becomes:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \dots \dots \dots (2)$$

(Shahryari 2010)

Where k_1 is the intercept and q_e is slope of the plots.

2.6.4 Pseudo second-order equation

The adsorption kinetic may also be described by pseudo second order equation. The rate of pseudo second order equation is dependent on the amount of solute adsorbed on the surface of adsorbent and the amount of adsorbed at equilibrium. The differential equation is generally given as follows (Shahryari *et al.*, 2010):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \dots \dots \dots (3)$$

Where the pseudo second order kinetics rate constant is k_2 (g/mg.min) then the above equation (3) after taking integral becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{t}{q_e} \dots \dots \dots (4)$$

The value of q_e and k_2 can be determined experimentally from the slope and the intercept of the plots $\frac{t}{q_t}$ versus time (t) respectively.

Difference b/n Pseudo first order and Pseudo second-order

The main difference between a First Order Reaction & a Pseudo First Order reaction is that the Pseudo first order reaction is a reaction that should actually happen by some higher order (higher than 1) but occurs by first order because the concentration of one reactant used is very high &

another reactant used is very low. The concentration of the reactant which is very low can be neglected & thus the concentration of the reactant which has higher concentration is alone taken. This makes the reaction follow a first order kinetics rather than some higher order. This is Pseudo First order reaction. If your kinetic model best fits Pseudo first order reaction plot by giving r^2 value close to 1, it indicates that the reaction is more inclined towards physisorption. Similarly if the reaction fits well to Pseudo second order model it indicates an inclination towards chemisorption. Several reactions in general follow chemisorption initially and that too over a very short period of time.

2.7 Thermodynamic Parameter of adsorption studies.

The thermodynamic property of PSP for MB adsorption was investigated at varying reaction temperature. The following were employed to elucidate the mechanism of MB removal by PSP:

$$\ln K_2 = \ln A - \frac{E_a}{RT} \dots\dots\dots(5)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots(6)$$

Where, T, R, K are represented as the temperature (K), gas constant (8.314 J/mol K), and equilibrium constant respectively (Zaki, *et al.*, 2000) . Where K can be obtained from:

$$K = \frac{C_{ads}}{C_e} \dots\dots\dots(7)$$

$$\Delta G^0 = -RT \ln K \dots\dots\dots(8)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \dots\dots\dots(9)$$

Where K = equilibrium constant

C_{ads}= amount of dye adsorbed on the activated carbon at equilibrium

C_e = equilibrium dye concentration mg/g

ΔG^0 = Change in Gibbs free energy

ΔH^0 = Change in enthalpy ΔS^0 = Change in entropy

3. MATERIALS AND METHODS

3.1 Study Sites and Description

Synthesis of activated carbon (AC) prepared from PSP (adsorbent) and all batch adsorption experiments were carried out at Adama Science and Technology University in Chemistry Laboratory.

3.2 Chemicals.

The following chemicals were used: Hydrochloric acid (HCl) (MW 36.46g/mol, Min, assay 35-38%) sodium hydroxide (NaOH) (MW 41.36g/mol), Ethanol (CH₃CH₂OH) (MW 46.37g/mol), potassium hydrogen phthalate (C₈H₅KO₄) (MW 204.22g/mol, Loba Chemie), sodium tetra borate (Na₂B₄O₇) (MW 381.37g/mol, Buiux Labortory), sodium dihydrogen phosphate (NaH₂PO₄) (MW 156.0 g/mol. Alpha chemika), and potassium chloride ,KCl(MW 64.8 g/mol,). All chemicals were used of analytical reagent grade. Methylene blue (MB) (MW319.859 g/mol basic blue 9), dye and distilled water were used for preparation of stock solution. HCl and NaOH were used to adjust the pH of the solution. Distilled water was used for experimental studies.

3.3 Instruments

The following were the instruments used during the adsorption experiments.

UV-VIS spectrometry (SANYO SP65 GALANA KAMP,UK), PH meter (mettler ToledoMp220), Oven (Contherm 260 M) Mechanical agitator (shaker)(Orbital shaker SOL,UK),muffle furnace (BiBBY,stuart), thermometer, ceramic crucible, whatman No 1 filter paper and desiccators

3.4 Methods and Procedures

3.4.1 Collection of palm seeds samples

Sufficient quantities of PSP were used for preparation of AC. The palm seeds were collected from Arsi Negele district in Eastern Arsi Zone of Oromia Region, Ethiopia. Clean plastic bags were used to carry the palm seeds samples to Adama Science and Technology University, Chemistry Laboratory.

3.4.2 preparation of activated carbon from palm seeds as adsorbent

The palm seeds collected from Arsi-Negelle district were dried in sun light until they became moisture free. The sample was washed several time with distilled water and ethanol in the laboratory to remove color, dirt and organic materials such as (protein, fat and soluble carbohydrate). The washed palm seeds used as adsorbent were dried in a convection oven at temperature 100°C - 110°C for 24 hours to eliminate the bulk of the volatile matter. Then the dried palm seeds were ground using domestic grinder and then were sieved using standard sieve with matrix size of 75-300 μm to obtain fine powder of uniform particle size. Then transferring the palm seeds powder to 250 ml beaker, and was soaked with sufficient amount of concentrated HCl and left overnight at room temperature in order to: extract the compound formed and reagent excess and degrade or dehydrate the organic molecules during carbonization that prevent deposition of hydrocarbon on the carbon surface. The acid treated palm seeds of powder was then washed thoroughly with distilled water and then filtered with Whatman number one filter paper. The residue was transferred into a clean beaker, to which enough amount of 0.1M NaOH solution was added and soaked again overnight so that any excess acid present was neutralized. The treated solid residue was washed again with distilled water till attaining a constant pH and then made to dry at room temperature. The powder obtained was kept in a hot air Oven at 100°C for a day. The impregnated precursor was carbonized in a horizontal tubular furnace under nitrogen flow with a heating rate of $5^{\circ}\text{C min}^{-1}$, to allow free evolution of volatiles, up to the hold temperature for 1 h. (Baker,1998,and Amri, 2008), then The remaining

PSP (activated carbon) were then cooled and stored in desiccators for later use for adsorption studies.



Palm seeds without cover



ground palm seeds sieved palm seeds powder

PSP heated in muffle furnace

Figure 3. 1 Adsorbent preparation process

Carbonization, the conversion of organic matter to elemental carbon at high temperature in an inert atmosphere is the first stage in the physical activation process. This results in the elimination of elemental hydrogen and oxygen in the precursor to produce a carbon skeleton possessing a latent pore structure. (Baker, 1998, Amri, 2008) Typical temperatures for the carbonization step ranges from 500⁰C to 900⁰C (Yeganeh, 2006 and, Kaghazchi, *et al.*,2006).

3.4.3 Determination of physiochemical properties of the PSP adsorbent

3.4.3.1 Determination of the moisture content of the adsorbent

One gram of adsorbent was weighed accurately in an evaporating dish and placed in an electric oven at 110⁰C for 2 hr. it was then cooled and weighed again. The process of heating, cooling

and weighing of the material was repeated several times at 30 min intervals until the difference between two consecutive weighing become less than 0.01g (Renugadevi *et al.*, 2011). 0.01g indicates how much the weighed adsorbents are near to each other. The moisture content was determined using equation 10 below:

$$\text{Moisture content by weight} = \frac{(M-X)}{M} \times 100 \dots\dots\dots (10)$$

Where M is weight of adsorbent taken for the test (g) and X is weight of adsorbent after drying both in grams

3.4.3.2 Determination of the ash content

One gram of adsorbent was weighed accurately in a porcelain crucible and placed in an electric oven at 110⁰C for 2 hours. The adsorbent kept in a porcelain crucible in an electric oven was then removed from the oven & heated in a muffle furnace at a temperature of 500⁰C for 2 hours. The crucible with its content was removed from the furnace and cooled to room temperature and weighed again. The process of heating, cooling and weighing of the material was repeated several times at 30 min intervals until the difference between two consecutive weighing become less than 0.01g (Baker, 1998, and Amri *et al.*, 2008). The ash content was determined using equation 11 below:

$$\text{Ash content percent by weight} = \frac{M_1}{(M_2-x)} \times 100 \dots\dots\dots (11)$$

Where M₁ is weight of the ash (g),

M₂ is weight of adsorbent taken for the test (g) and

X is weight of adsorbent after drying both in grams moisture content present in the material taken for test.

3.4.3.3 Preparation of adsorbate (Stock Solution preparation)

Preparations of stock solution of methylene blue was carried out by dissolving 1gm of (MB) in 1000 ml of distilled water in order to get 1000 ppm concentration, while the working concentrations were prepared by using the equation.

$$C_1 V_1 = C_2 V_2 \dots\dots\dots (12)$$

The concentration of MB was measured using UV-visible spectrometer. A calibration curve is plotted between absorbance and concentration of dye solution to obtain absorbance concentration profile.

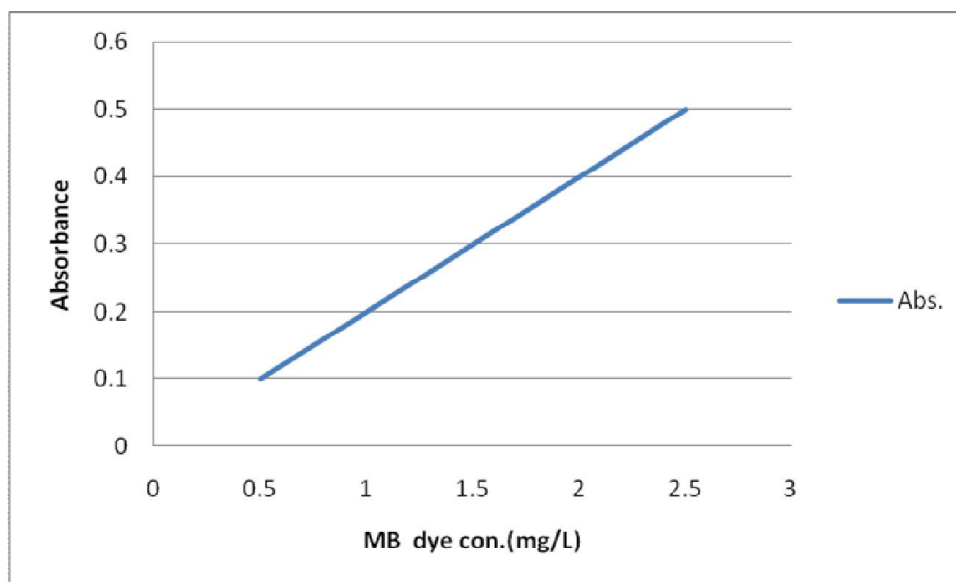


Figure 3.1: Calibration curve for MB

3.5 Adsorption Studies

The experiments on the adsorption of MB, on AC prepared from PSP were conducting out in reciprocating shaker at 200 rpm using 100mL of flasks an aqueous solution of the dye in concentration of 25mg/L , 50 mg/L, 75 mg/L, and 100 mg/L. To the resulting solution, 300mg of adsorbent was added to each 100 ml flask at a neutral pH and room temperature. The initial pH value of each solution was adjusted with 0.1M HCl or 0.1M NaOH using a pH meter. In all experiments the flasks were sealed to prevent any change in volume during the experiment. After shaking the flasks, 5ml samples was withdrawn at 15 min intervals from the flasks and each time the dye solution was first separated from the adsorbent by centrifuging at 200 rpm for 10 min at room temperature until equilibrium was reached. After equilibration time, the adsorbents and the supernatant solution were separated by filtration. After filtration, the concentration of MB, in the supernatant solution was analyzed using an Uv.-visible spectrophotometer by recording the absorbance changes at a wavelength of maximum absorbance (664nm). The percentage removal of dye (adsorption) and amount of dye adsorbed on adsorbents at equilibrium was calculated by equation (13) and (14) respectively.

$$\text{Removal efficiency (\%)} = \frac{[(C_0 - C_e)]}{C_0} \times 100 \dots\dots\dots(13)$$

$$q_e = \frac{[(C_0 - C_e)]}{C_0} \times \frac{V}{M} \dots\dots\dots(14)$$

Where, C_0 = Concentration of MB, dye in the sample solution before treatment

C_e = Concentration of MB, dye in the sample solution after treatment

q_e = amount of MB, dye absorbed on adsorbents at equilibrium.

V = volume of MB solution.

M = mass of adsorbent (PSP)

The effects of various parameters such as pH, contact time, MB, dye concentration, adsorbent dosage, ionic strength and temperature on adsorption of MB onto activated carbon prepared from PSP were studied.

3.6. Effects of various parameters on the adsorption of MB, PSP

3.6.1 Effect of initial dye concentration

In order to investigate the effect of initial dye concentration on 300 mg of AC prepared from PSP was added to different MB, dye concentrations (25 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm) which were prepared from the dye stock solution in 100 ml flasks. All of the samples were agitated on shaker for 30 minutes. 5 ml of the solution (sample) was taken from each of the solution at 10 min interval from the flask. Finally the concentration of MB, solution free from any suspended carbon was estimated by measuring its absorbance at 664 nm using UV-Vis spectrophotometer by kept other parameters constant.

3.6.2 Effect of adsorbent dosages

In order to determine the effect of adsorbent dosage 25 ppm MB, dye concentration was added to different AC prepared from PSP doses (50, 100, 200 and 300 mg) in a 100mL flask and agitated under mechanical shaker for 30 minutes. 5 ml of the solution (sample) was withdrawn from the flask at 10 min interval and the absorbance was measured using UV-VIS at 664 nm.



Figure 3. 2 Palm seeds before and after MB adsorption.

3.6.3 Effect of solution pH

The influence of solution pH (2-10) was examined to understand the adsorption mechanism. 100 ml of the dye solution was mixed with constant concentration of AC prepared from PSP (300mg) at 200 rpm in a 100ml flask and agitated under mechanical shaker. 5 ml of this solution (sample) was withdrawn at 10 min interval from the flask and the absorbance was measured using UV-VIS at 664 nm.

3.6.4 Effect of ionic strength

In order to investigate the effect of ionic strength on the potential of AC prepared from PSP, each KCl concentrations (50 ppm, 100 ppm, 150 ppm and 200 ppm) was added to 20 ml of dye solution (10ppm) in existence of 300 mg AC prepared from PSP after 60 min. All of the samples were agitated on shaker for 30 minutes. 5 ml of the solution (sample) was taken from each of the solution at 10 min interval from the flask. Finally the absorbance was measured using UV-VIS at 664 nm.



Figure 3. 3 Dye solution before and after adsorption process with MB.

3.6.5. The effect of temperature

The effect of temperature was tested on the potential of AC prepared from PSP by mixing 25 ppm dye solution with 300 mg AC prepared from PSP in 100 ml small conical flask in thermostat water bath under mechanical shaker at varying temperature 25, 50, and 75⁰C. 5 ml of this solution (sample) was withdrawn at 10 min interval from the flask and the absorbance was measured using UV-VIS at 664 nm by keeping other parameter constant Finally the amount of MB, adsorbed and percent removal of MB, dye were calculated and the plot of percent removal of MB, dye as well as the amount of MB, dye adsorbed were plotted.

3.6.6 The effect of contact time.

The effect of contact time was tested on the potential of AC prepared from PSP by mixing 300mg of the AC prepared from PSP with different initial concentration (25, 50, 75 and 100mg/L) of MB, solution in 100 mL flask for 10 – 60 min 5 ml of this solution (sample) was withdrawn at 10 min interval from the flask and the absorbance was measured using UV-VIS at 664 nm by keeping other parameter constant Finally the amount of MB, adsorbed and percent removal of MB, dye were calculated and the plot of percent removal of MB, dye as well as the amount of MB, dye adsorbed were plotted.

3.7 Data Analysis and Interpretations

All data generated from the above experiments were analyzed using the Micro soft Excel, window program and the linear regressions values were computed as required.

4. RESULTS AND DISCUSION

4.1 Adsorption Parameters

4.1.1. The effect of the contact time on MB dye adsorption

Figure 4.1 indicates that after determination of moisture and ash content of AC prepared from PSP when 300mg of the AC prepared from PSP was added to different initial concentration (25, 50, 75 and 100mg/L) of MB, solution in 100 ml flask for 10 – 60 min and agitated all samples on shaker for 30 minutes and after filtration, withdrawn 5 ml of sample from the flask by measured the absorbance using UV-VIS at 664 nm, the percentage removal of MB, dye was increased with an increase in contact time before equilibrium was reached. Other parameters such as adsorbent dosage: 300 mg, pH: 7, temperature: 298 K, were kept constant. The result indicates that MB, dye removal was increased with the contact time variation increased from 10 to 60 minutes. From 60 and above 60 minutes the percent removals of MB remain constant for all initial concentration of MB dyes, which showed that equilibrium was reached at 60 minutes itself. Thus the results illustrate that the optimum contact time for maximum removal (95.90%), of MB, dye was 60 minutes. This shows that equilibrium can be assumed at 60 min since the value of $\ln(q_e - q_t) = 0$ (Appendix Table 1.6). The result presented in (Figure 4.2) indicates that the adsorption capacity at equilibrium increases from 4.00 to 16.50 mg/g whereas the percentage removal of dye decreased from 95.90 to 41.69% with an increase in initial concentration of MB, dye. The adsorption capacity and rate of percent removal are higher at the beginning due to large surface area of the adsorbent available for the adsorption of the dye more quickly at low concentration and later case the available adsorption sites are saturated unable to accommodate the higher concentration of the adsorbate (Baek, 2010). During, the experiment carried out, a great color reduction was observed at contact time of 60 min to achieve equilibrium. This result is important because equilibrium time is one of the important parameter for an economical wastewater treatment system. Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption of MB. The theoretical Langmuir adsorption isotherm is often used to describe adsorption of a solute from a liquid solution.

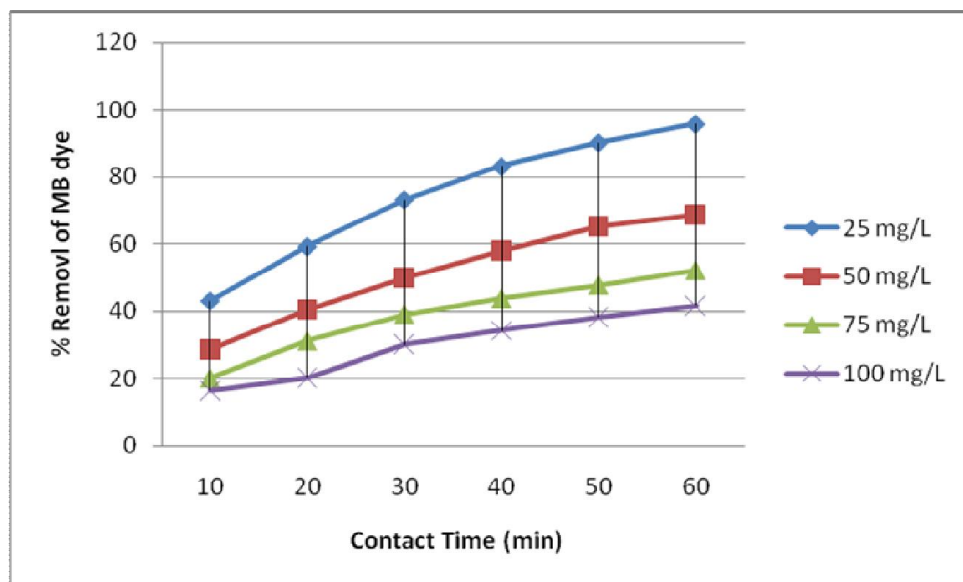


Figure 4. 1. Effect of the contact time on the sorption capacity of MB onto AC prepared from PSP

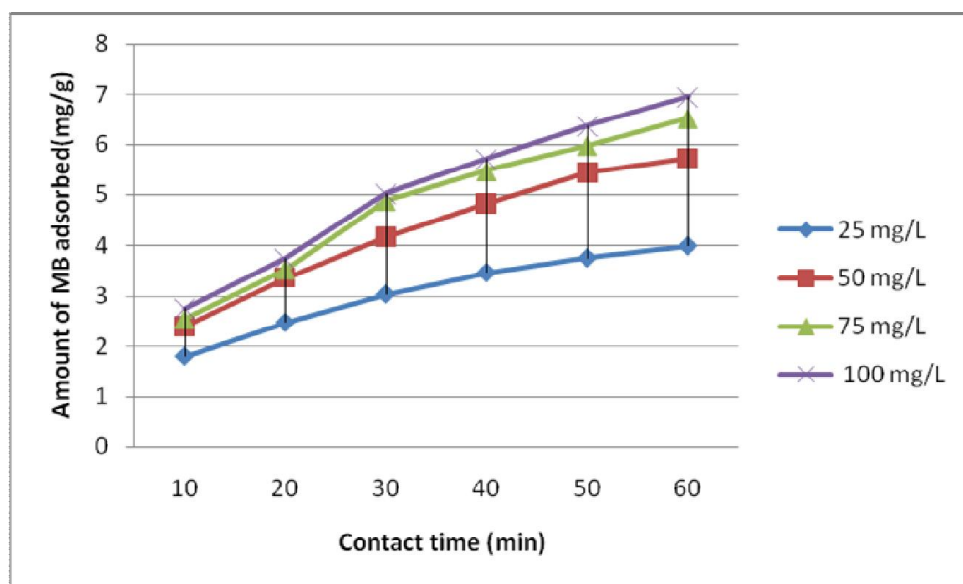


Figure 4. 2 Effect of the contact time on the sorption capacity of MB, dye onto AC prepared from PSP

4.1.2 Effect of initial concentration on MB adsorption

The effect of initial concentration on the adsorption of MB on AC prepared from PSP was studied in the range (25-100 mg/L). The result presented in (Figure 4.3) indicates that after determination of moisture and ash content of AC prepared from PSP When 300 mg of AC prepared from PSP was added to different MB dye concentrations (25 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm) in 100 ml flasks and agitated all samples on shaker for 30 minutes and after filtration, withdrawn 5 ml of sample from the flask by measured the absorbance using UV-VIS at 664 nm, the percentage removal of MB dye decreased from 67.40% to 32.28% with increasing in initial concentration of MB dye due to the fixed total number of adsorbent available sites, given adsorbent dose adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of the adsorbate. While the amount of MB adsorbed increases from 2.808 mg/g to 5.38 mg/g with increase of dye initial concentration) due to the increased ratio of number of moles of MB dye to the vacant available sites (Yadav *et al.*, 2011). (Appendix Table 1.1). For a given adsorbent dose the number of adsorbent available sites was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of the adsorbate, consequent to an increase in initial MB concentration (Yadav *et al.* 2011). Therefore it was evident from the results that MB L adsorption was dependent on the initial MB concentration.

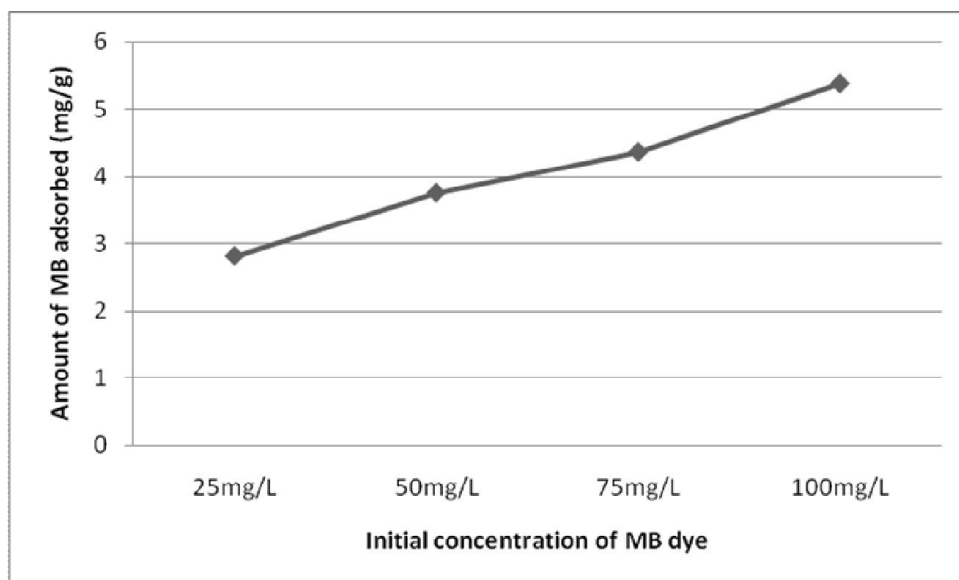


Figure 4. 3 Effect of the initial dye concentration on the sorption of MB dye onto AC prepared from PSP.

4.1.3 The effect of PSP dosage on MB adsorption

Adsorption efficiency of MB dye adsorption was studied by varying the amount of adsorbents from 50 mg to 300 mg keeping other parameters (pH and contact time) constant. The result of Figure 4.4 reveals that after determination of moisture and ash content of AC prepared from PSP when 50 ppm of MB dye concentration was added to different doses AC prepared from PSP (50, 100, 200 and 300 mg) in a 100 ml flask and agitated all samples on shaker for 30 minutes and after filtration, withdrawn 5 ml of sample from the flask by measured the absorbance using UV-VIS at 664 nm, the percent removal of MB dye usually increased with increasing PSP dosage due to increased surface area and active functional group. From the Figure 4.4 it is clear that no further increase in adsorption after a certain amount of adsorbent was added (300mg). The maximum percentage removal of MB dye was about 80.74% at the PSP dosage of 300 mg (Appendix Table 1.2). This result also suggest that after a certain dose of AC prepared from (PSP) or adsorbent, the equilibrium conditions reached and hence the amount of MB bound to the adsorbent and the amount of MB in the solution remain constant even with further addition of the dose of AC prepared from PSP (Baek *et al.*,2010).

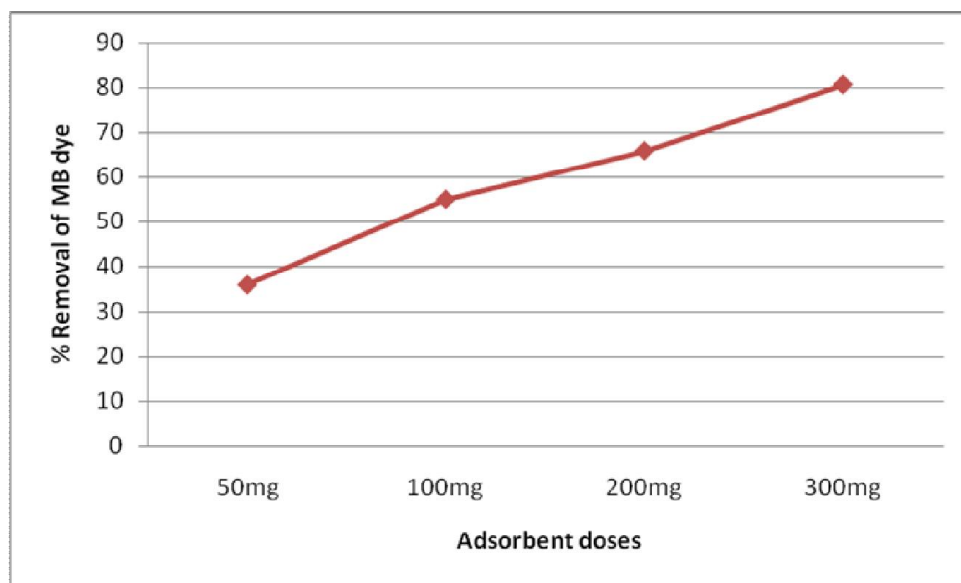


Figure 4. 4 Effect of the adsorbent dose on the sorption capacity of MB dye onto AC prepared from PSP.

4.1.3 Effect of pH on the adsorption of MB dye

The effect of pH on the adsorption of MB dye on AC prepared from PSP is represented in Figure 4.5. The result reveals that, after determination of moisture and ash content of AC prepared from PSP, when 25ppm of MB dye was mixed with 300mg of AC prepared from PSP in a 100 ml flask and agitated all samples on shaker for 30 minutes and after filtration, withdrawn 5 ml of sample from the flask by measured the absorbance using UV-VIS at 664 nm, the selected adsorbent showed good adsorption capacity more in basic medium than in acidic medium (Appendix Table 1.3). This may be attributed to the cationic nature of the AC which led to adsorb hydrogen ions (H^+) on the surface of it when immersed in water and make it positively charged. From Figure 4.5 it is evident that the optimum removal of color was observed at pH =7 and minimum at pH= 2. At pH = 2 the removal of MB dye was minimum but it increased along with increasing initial pH of the dye solution from 2 to 6, and the maximum uptake capacity was attained at pH 7. The observed increase in adsorption of MB dye at higher pH may suggest that the carbon surface is negatively charged which favor adsorption of cationic dye on the available sites. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged cationic dye due to electrostatic repulsion. At pH above 7.0, no substantial uptake was observed and this could as a result of saturation of the actives site or low stability of the dye molecules at higher pH as reported elsewhere (Gecgel *et al.* , 2013). Further increase in pH causes a drastic decrease in the adsorption percentage. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent which ultimately leads to the reduction in sorption capacity.

At pH = 2 lowest adsorption of MB dye may be occurred because the surface of activated carbon from palm seeds powder is positively charged which led to an increase in hydrogen ion concentration which compete with the positively charged carbon surface and adsorption of the positively charged dye decreases because of reduction in the force of attraction between adsorbate and adsorbent (Ponnusami, 2009). Moreover, the increase in the adsorption of MB dye with increasing of pH value is also due to electrostatic attraction between cationic dye and excess OH^- ions in the solution.

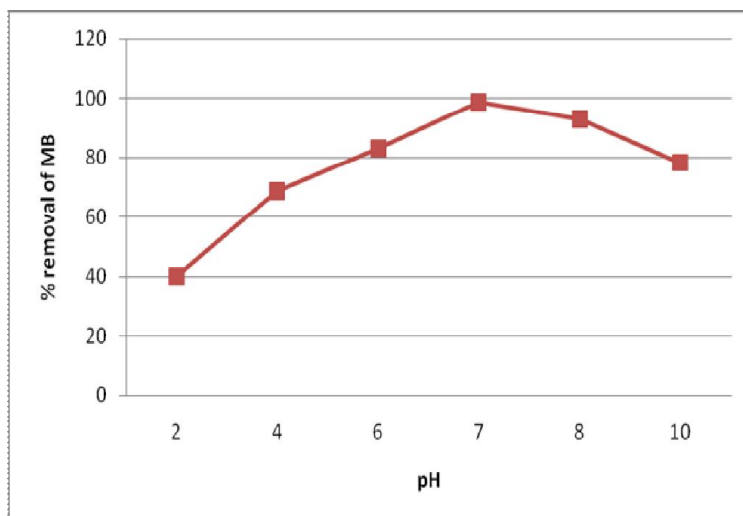


Figure 4. 5 Effect of the PH on the sorption of MB onto AC prepared from PSP.

4.1.4 Effect of ionic strength

The effect of ionic strength was also conducted at different salt concentration as shown in Figure 4.6. The result indicates that after determination of moisture and ash content of AC prepared from PSP when different KCl concentrations (50 ppm, 100 ppm, 150 ppm and 200 ppm) was added to 25 ppm of dye solution in existence of 300 mg AC prepared from PSP and agitated all samples on shaker for 30 minutes and after filtration, withdrawn 5 ml of sample from the flask by measured the absorbance using UV-VIS at 664 nm, the amount of MB dye adsorption by AC prepared from PSP decreased with increasing ionic strength as shown in Figure 4.6 (Appendix Table 1.5). This result may be because of competition for adsorption a site between K^+ ions and MB, similar observation has been reported (Ghosh 2013).

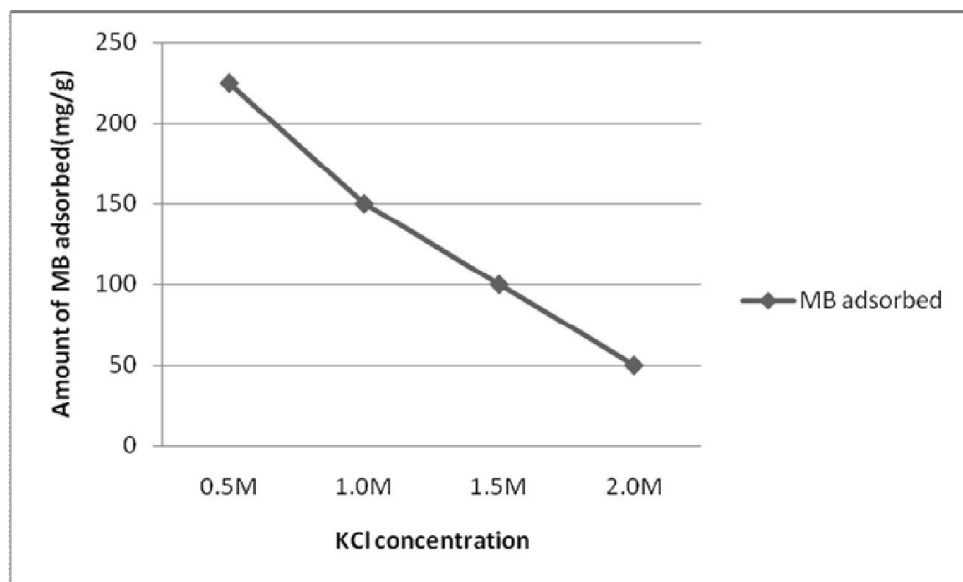


Figure 4. 6 Effect of KCl salts concentration on the sorption of MB dye onto AC prepared from PSP.

4.1.5 Effect of temperature on the adsorption of Methylene blue

The adsorption process of MB dye was also conducted at different temperatures (25°C , 50°C and 75°C) using 300 mg AC prepared from of PSP and MB concentration of 25 mg/L as shown in Figure 4.7. The result indicates that after determination of moisture and ash content, when 25 ppm dye solution was mixed with 300 mg AC prepared from PSP in 100 ml small conical flask in thermostat water bath at varying temperature from 25°C to 75°C and agitated all samples on shaker for 30 minutes and after filtration, withdrawn 5 ml of sample from the flask by measuring the absorbance using UV-VIS at 664 nm, the adsorption capacity of MB dye onto AC prepared from PSP increased from 5.93 mg/g to 7.45 mg/g. Therefore the higher temperature facilitated the adsorption of MB dye on AC prepared from PSP. The result of Figure 4.8 indicates that, the percent removal of the adsorbate on the adsorbent increased with increase in temperature of the system from 25°C to 75°C and adsorption capacity of the adsorbent decreased with increase in temperature of the system from 25°C to 75°C (Appendix Table 1.4). The obtained data also indicated that the rate of MB removal increased steadily with temperature increase until 60 minutes, after which no substantial up take was observed and this may be attributed to decreasing free active sites on AC prepared from PSP with time. The increased adsorption with the increase

in temperature showed that the treatment process is endothermic in nature and may be ascribed to enhanced tendency of the MB dye molecules to escape from the bulk media to the activated carbon prepared from PSP phase (Chiou, and Li *et al.* , 2003).

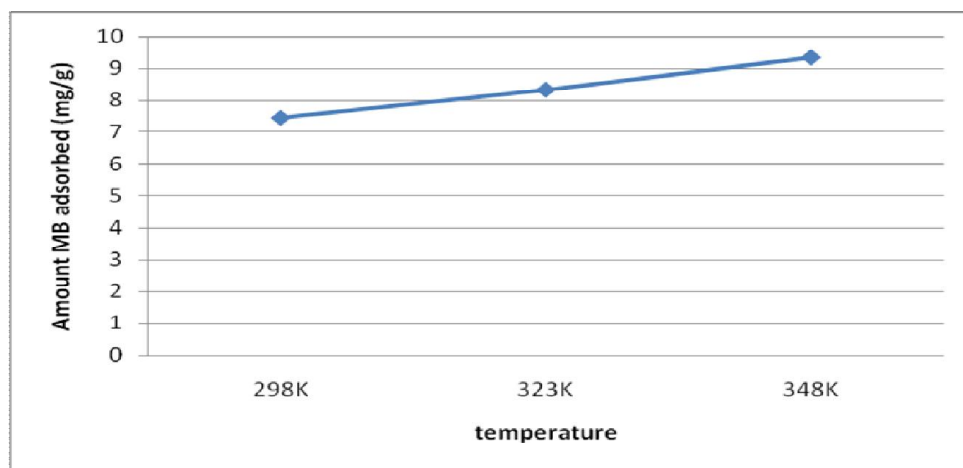


Figure 4. 7 Effect temperature on the sorption of MB dye onto activated carbon prepared from PSP.

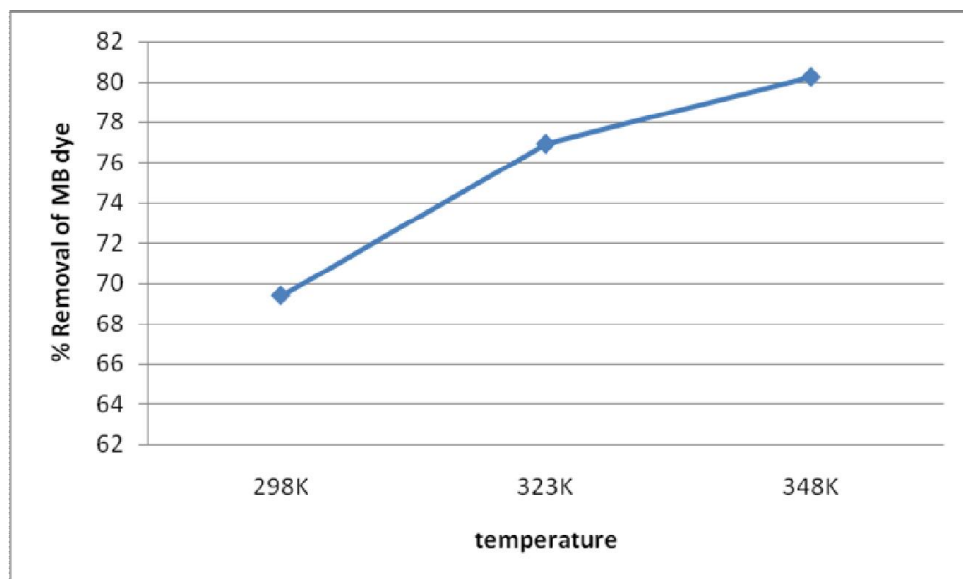


Figure 4. 8 Effect of temperature on the sorption of MB dye onto AC prepared from PSP

4.2 Kinetics of the Adsorption

4.2.1 Pseudo first order kinetics

Lagergren's kinetic equation describes the adsorption of liquid solid systems based on solid capacity. In order to distinguish kinetic equation based on concentration of solution and adsorption of a solid, Lagergren's first order rate equation was applied (Baek *et al.*, 2010). A plot of $\ln(q_e - q_t)$ versus time (t) described in the literature part (section 2.8.1 equation 1) gives linear line curve as shown in Figure 4.9. From this curve the values of k_1 and q_e were determined using the slope and intercepts of the line respectively and these values are presented on the Table 4.1. As it can be observed from Table 4.1 that the experimental data were noticed not to match with the pseudo first order kinetics with lower R^2 values obtained at various concentrations investigated. It is concluded that the adsorption process cannot be explained by this model (Baek *et al.*, 2010).

Table 4. 1 Kinetic parameters for the adsorption of MB on to PSP

Initial concentration(mg/L)	Pseudo first order kinetics		
	$K_1 \text{min}^{-1}$	$q_e(\text{cal})\text{mg/g}$	R^2
25	6.921	6.560	0.99015
50	5.297	8.138	0.97361
75	5.058	9.160	0.72996
100	5.758	11.166	0.9603

K = slope and

q_e = intercepts.

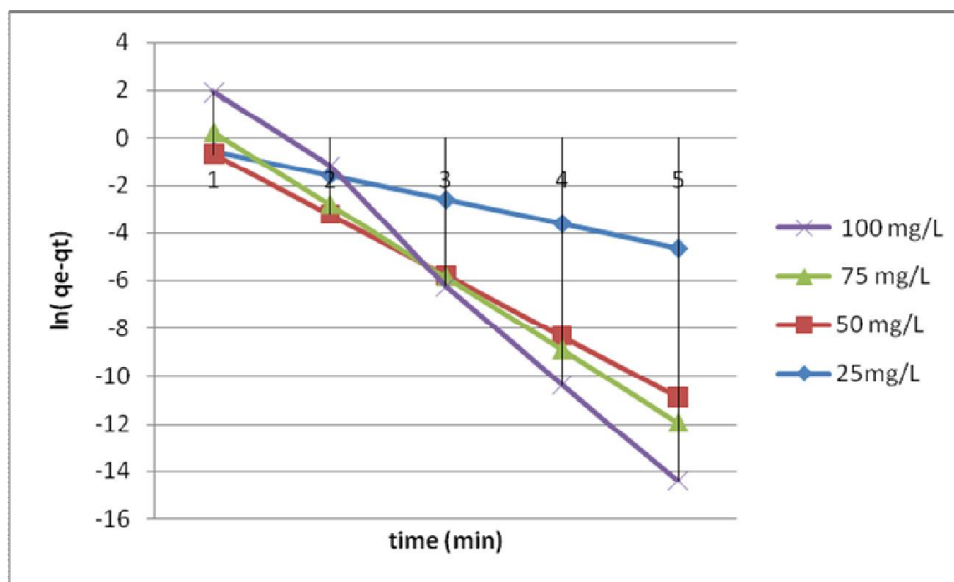


Figure 4. 9 Pseudo first Order kinetics plots for the sorption of MB dye onto PSP.

4.2.2 Pseudo second order kinetics

The pseudo second order adsorption rate equation usually considers the adsorption capabilities of solids. A plot of t/q_t versus t described in literature (section 2.8.2 equation 4) give a linear relationship as depicted in Figure 4. 10 at initial concentration of 25, 50, 75 and 100 mg/L, PH =7, adsorbent dosage = 300 mg/100 ml of MB solution, contact time=60 min, agitation speed=200 rpm, particle size 75-300 μm . Accordingly the value of q_{e2} = slope and k_2 = intercept were determined similarly from the plot, respectively and the values obtained as such are presented in Table 4.2. The equilibrium adsorption capacity, q_{e2} , increased from 8.22375 to 15.24375 mg/g when the initial concentration of the dye has increased from 25 to 100 mg/L (Table 4.2). This is indicative of the fact that the dye removal is highly dependent on dye initial concentration and pseudo-second order model may be the most suitable to describe the adsorption of MB onto PSP. While the initial concentration varies from 25 to 100mg/L the rate constant k_2

decreases from 8425×10^{-3} to 349875×10^{-5} g/mg.min. Similar results reported on the adsorption of MB onto dehydrated wheat bran carbon (Ozer and Dursum *et al.*,2007).

Table 4. 2 Kinetic parameters for the adsorption of Methylene blue on to PSP

Initial concentration(mg/L)	Pseudo second order kinetics		
	$K_2 \text{min}^{-1}$	$q_e(\text{cal})\text{mg/g}$	R^2
25	8.425	8.224	0.99912
50	3.386	10.682	0.98033
75	3.182	12.621	0.99512
100	3.499	15.244	0.98362

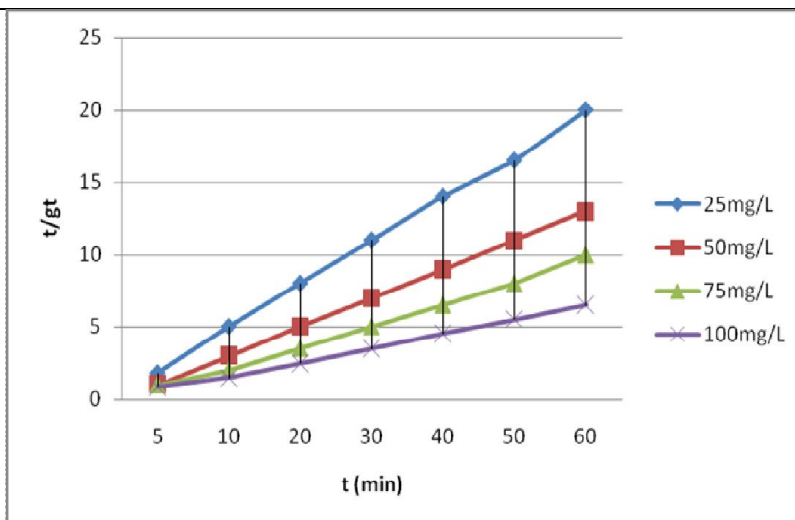


Figure 4. 10 Pseudo-second order kinetics plot for the sorption of MB dye onto the palm seeds powder PSP.

4.2.3 Thermodynamic properties

The thermodynamic properties of PSP for MB adsorption were investigated at varying reaction temperature. Thermodynamic parameters such as the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), were calculated from the variation of the thermodynamic equilibrium constant, K , with temperature. Free energy change, ΔG^0 of the adsorption reaction is given by, $\Delta G^0 = -RT \ln K_d$ where K_d is distribution constant. The values of K and others

thermodynamic parameters for the adsorption process were calculated using (Dogan, *et al.*, 2000) and the value of ΔH , ΔG , and ΔS for initial concentration of 25, 50, 75 and 100 mg L⁻¹ are shown in the Table 4.3. The negative value of ΔG indicates the feasibility of and the spontaneous nature of the MB dye adsorption on AC prepared from PSP. The magnitude of ΔG increased with increasing temperature, revealing that the degree of spontaneity increased at higher temperatures. The positive values of ΔS reflect an increased degree of disorderliness at the solid/liquid interface during the adsorption of MB dye onto PSP. The Positive value of ΔH shows the endothermic nature of dye adsorption (Vadivelan *et al.*, 2005).

Table 4. 3 Thermodynamic parameters for the adsorption of MB on to PSP

Temperature (K)	ΔG^0 (kJ/mol.)	ΔH^0 (kJ/mol.K)	ΔS^0 (kJ/mol.)
298	-3.359	3.361	0.0047
323	-3.641	3.563	0.241
348	-3.923	3.924	0.0029

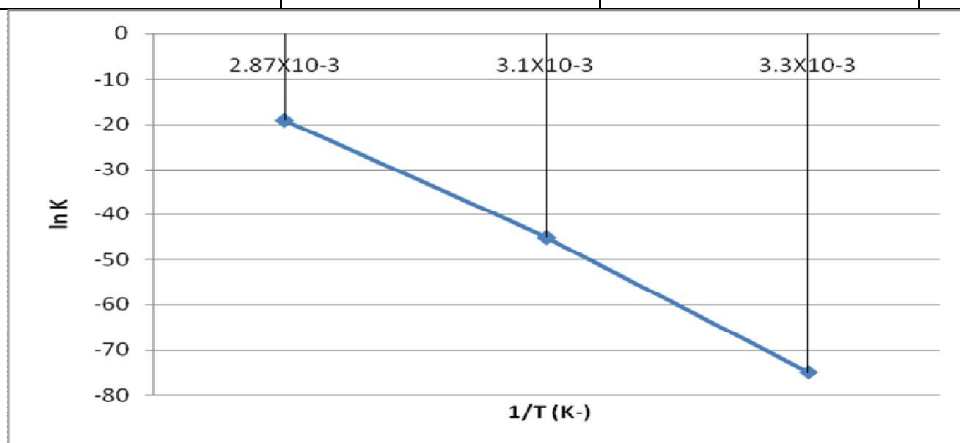


Figure 4. 11 Effect of Temperature on the adsorption of MB onto activated carbon prepared from PSP.

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

In the present work, a low cost adsorbent was prepared, characterized, its adsorption capability was estimated and the following conclusions could be drawn:

- ☞ The study indicates that the AC prepared from PSP might be used as an adsorbent for the removal of MB dye from wastewater.
- ☞ The adsorption process in the removal of MB dye from wastewater using AC prepared PSP was strongly based upon various parameters such as initial dye concentration, adsorbent dosage, pH, contact time, and temperature.
- ☞ The percent removal of MB dye decreases as the dye initial concentration increases. However, the amount of dye adsorbed increases with increase in dye initial concentration.
- ☞ The adsorption capacity is dependent on pH solution, contact time, adsorbent dosage and adsorbate concentration. The maximum percentage removal of MB was attained at 60 minute.ie (95.90%).
- ☞ The time concentration profiles and the equilibrium isotherm studies showed that AC prepared from PSP can be effectively used for the removal of MB from wastewater.
- ☞ The adsorption capacity of AC prepared from PSP increased with the increase in pH and initial MB dye concentration.
- ☞ Thermodynamic parameter of adsorption studies revealed that the adsorption MB using AC prepared from PSP is endothermic in nature; hence it can be concluded to be physical adsorption phenomenon.

5.2 Recommendations

1. As this research done on the study of MB removal from wastewater using AC prepared from palm seeds powder, further work should carried out on effluents and its catchment by considering environmental matrices such as water, biota, and plants.
2. Simultaneously enhancing awareness of the community should be done on the possible effects of river water containing dye.

REFERENCE

- Agarwal S. , Tyagi I. , Gupta V. K. , Ghasemi N , Shahivand M , Ghasemi M., (2016). "Kinetics, equilibrium studies and thermodynamics of methylene blue adsorption on Ephedra strobilacea saw dust and modified using phosphoric acid and zinc chloride." *J. Mol. Liq.*, 218, 208–18.
- Ahmad, T., Danish, M. ,Rafatullah, A. ,Ghazali, O., Sulaiman, R. Hashim and M. Ibrahim (2012). "The use of date palm as a potential adsorbent for wastewater treatment: a review." *Environ. Sci. and Poll. Res.* 19(5): 1464-1484.
- Al-Degs Y.S, Khraisheh M. A. M , Allen S.J , Ahmad M. N., (2009). "Adsorption characteristics of reactive dyes in columns of activated carbon." *J. Hazard. Mater.*, 165, 944–9
- Allen, S.J. and Koumanova B., (2005), "Decolorization of water/ wastewater using adsorption" , (Review), *J. of the University of Chem. Techno. and Metallurgy*, 40(3):175-192.
- Amri, N.B. (2008), "Preparation of Activated Carbons from Waste Tyres Char Impregnated with Potassium Hydroxide and Carbon Dioxide Gasification, M.sc." Thesis Submitted to the Department of *Chem. Eng.*, Universiti Sains Malaysia, 11 – 43
- Armagan B , Turan M , Celik M. S., (2004), "Equilibrium studies on the adsorption of reactive azo dyes into zeolite." *Desalination*; 170:33–9 .
- Baek, M. H., C. O. Ijagbemi,. Se-Jin O and Kim D. S. (2010). "Removal of Malachite Green from aqueous solution using degreased coffee bean." *J. Hazard. Mater.* 176(1-3): 820-828.
- Baker, F.S. (1998), " Kirk - Other Encyclopedia of Chemical Technology (CD): Activated Carbon "John Wiley and Sons, 4th Edition.
- Bhatnagar A , Sillanpa M. (2010) . "Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment." A review. *Chem Eng J*; 157(2-3):277–96 .
- Bielska, M. and Szymanowski, J., (2006). "Removal of methylene blue from wastewater using micellar enhanced ultrafiltration." *Water Research*, Vol. 40, pp. 1027-1033,
- Chiou M. S., and Li, H.Y.(2003). "Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads." *Chemosphere*, 50(801095-1105.
- Crini G (2005). " Non-conventional low-cost adsorbents for dye removal: a review." *Bioresour Technol*; 97:1061–85.
- Crini G., 2006, "Non-conventional low-cost adsorbents for dye removal: A review." *Bioresour Technol.*, 97, 1061–1085.

- Dogan, M., Alkan, M., and Onganer, Y., (2000). "Water Air and Soil pollution" 120 - 229
- Espantaleon A. G., Nieto J.A., Fernandez M. and Marsal A (2003). "Use of activated clays in the removal of dyes and surfactants from tannery wastewaters. *Appl Clay Sci*; 24:105–10 .
- Ghosh, R. K. and Reddy D. D. (2013). "Tobacco Stem Ash as an Adsorbent for Removal of Methylene Blue from Aqueous Solution: Equilibrium, Kinetics, and Mechanism of Adsorption." *Water Air and Soil Pollution* 224(6).
- Gupta, V. and Suhas, K., (2009). " Applications of low cost adsorbents for dye removal: A review. " *J Environ Manag*;90:2313–42 .
- Itodo, H.U. and Itodo, A.U., (2010) "Surface coverage and Adsorption study of the dye uptake by derived acid and base treated mango seeds shells." *J. of Chem. and Pharmaceut. Rese*
- Mohan D, Singh K. P, Singh G. and Kumar K., (2002). "Removal of dyes from wastewater using fly ash, a low-cost adsorbent. " *Ind Eng Chem Res*;41:3688–95 .
- Morais L. C., Freitas O. M., Gonçalves, E. P, Vasconcelos, L. T., GonzalezBeca, C. G., (1999). "Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: variables that define the process." *Water Res*;33:979–88.
- Namasivayam , (2001) Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. " *Waste Manag*;21:105–10
- Netpradit, S., Thiravetyan, P., Towprayoon S., (2003). "Application of "waste" metal hydroxide sludge for adsorption of diazo reactive dyes." *Water Res*; 37:763–72 .
- Ozdemir, O., Armagan, B., Turan, M., Celik, M. S., (2004). "Comparison of the adsorption characteristics of azo-reactive dyes on mesoporous minerals. " *Dyes Pigment*;62:49–60 .
- Ponnusami, V., (2009). "Adsorption of methylene blue on to Glumohar plant leaf powder: equilibrium, kinetics and thermodynamics analysis," *j. environ. Proto. Sci.*,1(5):711-726
- Rafatullah, Sulaiman M., O., Hashim R. and Ahmad A. (2010). "Adsorption of methylene blue on low-cost adsorbents: A review." *J. Hazard. Mater.* 177(1-3): 70-80.
- Rafatullah, M., T. Ahmad, A. Ghazali, O. Sulaiman, M. Danish and R. Hashim (2013). "Oil Palm Biomass as a Precursor of Activated Carbons: A Review." *Critical Reviews in Environ. Sci. and Technol.* 43(11): 1117-1161.
- Renugadevi, N., R. Sengeetha and P.Laitha, (2011)." Effectiveness of an economic adsorbent in the adsorption of MB from an industrial dyeing effluent." *Department of Chemistry. Advances in Appl. Sci. Res.*,2(4):629-641

Robinson T , Chandran B , Nigam P (2002).“Removal of dyes from a synthetic textile dye effluent by bio-sorption on apple pomace and wheat straw." *Water Res*; 36:2824–30 .

Robinson T , McMullan G , Marchant R , Nigam P (2001).“ Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. " *Bio resour Technol*; 77:247–55 .

Sarici-Ozdemir (2014) “Removal of methylene blue from Wastewater by Activated Carbon Prepared from Rice Husk”. *Ind. Eng. Chem. Res.* 45(14),1723

Soni M , Sharma A. K., Srivastava J. K., Yadav J. S., (2012) . “Adsorptive removal of Methylene blue dye from an aqueous solution using water hyacinth root powder as a low cost adsorbent. " *Int. J. Chem. Sci. Appl*;3(3):338–45.

Vadivelanet, V. and Kumar K. V. (2005). "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk." *J. Colloid Interf. Sci.*, 286(1): 90-100. 34

Wang S , Boyjoo Y , Choueib A , Zhu ZH (2005).“Removal of dyes from aqueous solution using fly ash and red mud". *Water Res*;39:129–38 .

Yadav, D. K., Tyagi and O.P. Yadav, (2011).”Equilibrium and kinetics studies on adsorption of aniline blue from aqueous solution on to rice husk carbon.” *Int. J. of Chem. res.*, 2:59-64

Yeganeh, M. M., Kaghazchi, T. and Soleimani, M. (2006),” Effect of Raw Materials on Activated Carbon,” *Chem. Eng. Technol.*, 29, 1-5

Zaki, A.B.,El-Sheikh, M.Y., Evans, J. and El safty, S. A., (2000).” Kinetics and mechanisms of the sorption of some aromatic amines on to amberlite” IRA-904 anion-exchange resin. *J. Colloid and Interf. Sci.*, 221,58-63.

APPENDICES TABLES

Appendix Table 1. 7 Effect of the initial dye concentration on the sorption capacity of MB onto PSP (volume of the MB dye solution: 100 ml, initial concentration of MB 25 ppm, pH: 7, temperature: 298 K.).

Initial conc. Of MB(mg/L)	Final conc. (C_t) of MB dye(mg/L)	Amount of MB dye adsorbed q_t (mg/g)	% Removal of MB dye
25	4.82	2.81	80.74
50	16.44	3.76	67.12
75	44.79	4.37	38.95
100	67.72	5.38	32.28

Appendix Table 1. 8 Effect of the adsorbent PSP dose on the sorption capacity of MB onto PSP (volume of the MB dye solution: 100 ml, initial concentration of MB 25 mg/L, pH: 7, temperature: 298 K.).

amount of Palm seed added	Final conc.of MB (mg/L)after addition of PSP	Amount of MB adsorbed q_t (mg/g)	% removal of MB
50mg	15.985	3.364	36.06
100mg	11.243	2.740	55.03
200mg	8.504	2.293	65.98
300mg	4.816	1.503	80.74

Appendix Table 1. 9 Effect of PH on the sorption capacity of MB onto PSP (volume of the MB dye solution: 100 ml, initial concentration of MB 25 ppm, pH: 7, temperature: 298 K.).

PH	Final conc.of MB dye C_t (mg/L)	Amount of MB dye adsorbed q_t (mg/g)	%Removal of MB dye
2	15.02	3.25	39.92
4	7.85	3.88	68.60
6	4.23	4.11	83.08
7	0.33	3.46	98.68
8	1.75	2.86	93.00
10	5.45	1.66	78.20

Appendix Table 1. 10 Effect of temperature on the adsorption of MB onto PSP at initial concentration of 25mg/L, 50 mg/L, 75 mg/L, 100 mg/L (volume of the MB dye solution: 100 ml, initial concentration of MB 25 ppm, pH: 7, temperature: 298 K, contact time 30 min, particle size: 75-300 μm)

Initial MB dye (mg/L)	Temperature					
	25 ⁰ C		50 ⁰ C		75 ⁰ C	
	AMB* q _t (mg/g)	% RMB*	AMB* q _t (mg/g)	% RMB*	AMB* q _t (mg/g)	%RMB*
25	7.45	69.40	8.35	76.92	9.35	80.24
50	6.87	44.60	7.54	53.95	8.36	62.63
75	5.64	33.99	6.45	40.82	7.23	50.65
100	3.74	77.77	3.99	39.98	4.87	42.86

Note AMB* = amount of MB dye adsorbed q_t (mg/g)

% RMB* = percent removal of MB dye

Appendix Table 1. 11 Effect of Ionic strength on the adsorption of MB onto PSP at initial concentration of 25mg/L, 50 mg/L, 75 mg/L, 100 mg/L (volume of the MB dye solution: 50 ml, initial concentration of MB 50ppm, pH: 7, temperature: 298 K, contact time 30 min).

KCl concentration (M)	Final conc.of MB(mg/L)	Amount of MB adsorbed q _t (mg/g)	% Removal of MB dye
0.05	3.32	3.61	86.72
1.0	7.79	2.87	68.84
1.5	10.65	2.39	57.4
2.0	16.06	1.49	35.76

Appendix Table 1. 12 the value of Kinetic parameters of adsorption of MB on AC prepared from PSP and experimental data at initial concentration of 25,50,75 and 100 mg/L, adsorbent dose .300mg/100mL of MB solution, contact time = 60 min, agitation speed=200 rpm, PH =7 and temperature 25°C

Time (min)	C _o (mg/L)	C _t (mg/L)	q _e (mg/g)	q _t (mg/g)	ln (q _e - q _t)	t/ q _t	% Removal of MB dye
10	25	14.27	4.00	1.79	0.79	5.59	42.92
	50	35.66	8.16	2.39	1.75	4.18	28.68
	75	59.79	12.33	2.54	2.28	3.94	20.28
	100	83.47	16.50	2.75	2.62	3.64	16.53
20	25	10.21	4.00	2.47	0.43	8.09	59.15
	50	29.75	8.16	3.37	1.57	5.93	40.63
	75	59.79	12.33	2.53	2.28	7.91	31.17
	100	83.47	16.50	2.75	2.62	7.27	19.26
30	25	6.73	4.00	3.04	-0.04	9.87	73.10
	50	25.00	8.16	4.17	1.38	7.19	50.00
	75	45.73	12.33	4.88	2.01	6.15	39.03
	100	69.9	16.50	5.02	2.44	5.80	30.10
40	25	4.21	4.00	3.47	-0.63	11.52	83.15
	50	20.97	8.16	4.84	1.20	8.26	58.05
	75	42.17	12.33	5.47	1.85	7.31	43.77
	100	65.79	16.50	5.70	2.32	7.02	34.21
50	25	2.43	4.00	3.76	-1.43	13.30	90.30
	50	17.31	8.16	5.44	1.00	9.19	65.38
	75	39.21	12.33	5.97	1.85	8.37	47.72
	100	61.83	16.50	6.36	2.32	7.86	38.18
60	25	1.03	4.00	4.00	-	15.00	95.90
	50	15.6	8.16	5.73	0.89	10.50	68.80
	75	35.86	12.33	6.52	1.76	9.72	52.18
	100	58.31	16.50	6.95	2.26	8.63	41.69